

**Relationships of trace gases and aerosols and the emission characteristics at Lin'an, a rural site in eastern China during spring 2001**

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**Abstract.** We present measurements of trace gases and fine aerosols obtained from a rural site in eastern China during February 18-April 30, 2001. The field program aimed to characterize the variations in aerosol and gaseous pollutant concentrations and the emission signatures from the inland region of eastern China in the spring season. The data included O<sub>3</sub>, CO, NO, NO<sub>y</sub><sup>\*</sup>, SO<sub>2</sub>, methane, C<sub>2</sub>-C<sub>8</sub> non-methane hydrocarbons (NMHCs), C<sub>1</sub>-C<sub>2</sub> halocarbons, and the chemical composition of PM<sub>2.5</sub>. The average hourly mixing ratios ( $\pm$  s.d.) of CO, SO<sub>2</sub> and NO<sub>y</sub><sup>\*</sup> were 677 ( $\pm$ 315) ppbv, 15.9 ( $\pm$ 14.6) ppbv, and 13.8 ( $\pm$ 7.2) ppbv, respectively. The mean daytime ozone mixing ratio was 41 ( $\pm$ 19) ppbv. The most abundant NMHC was ethane (3189  $\pm$  717 pptv), followed by

ethyne ( $2475 \pm 1395$  pptv), ethene ( $1679 \pm 1455$  pptv), and toluene ( $1529 \pm 1608$  pptv). Methyl chloride was the most the abundant halocarbon ( $1108 \pm 653$  pptv). The average concentrations of organic carbon and elemental carbon in PM<sub>2.5</sub> were  $21.5 (\pm 7) \mu\text{g}/\text{m}^3$  and  $2.5 (\pm 0.7) \mu\text{g}/\text{m}^3$ , respectively, and sulfate and nitrate levels were  $17.3 (\pm 6.6)$  and  $6.5 (\pm 4) \mu\text{g}/\text{m}^3$ , respectively. CO showed moderate to good correlation with  $\text{NO}_y^*$  ( $r^2=0.59$ ), OC ( $r^2=0.65$ ),  $\text{CH}_3\text{Cl}$  ( $r^2=0.59$ ), soluble potassium ( $r^2=0.53$ ) and many NMHCs, indicating contributions from the burning of biofuel/biomass. CO also correlated with an industrial tracer,  $\text{C}_2\text{Cl}_4$ , indicative of some influence from industrial sources.  $\text{SO}_2$ , on the other hand, correlated well with EC ( $r^2=0.56$ ) reflecting the contribution from the burning of coal. Ammonium was sufficiently abundant to fully neutralize sulfate and nitrate, indicating that there were strong emissions of ammonia from agricultural activities. Silicon and calcium had poor correlations with iron and aluminum, revealing the presence of source(s) for Si and Ca other than from soil. Examination of  $\text{C}_2\text{H}_2/\text{CO}$ ,  $\text{C}_3\text{H}_8/\text{C}_2\text{H}_6$ , nitrate/(nitrate+ $\text{NO}_y^*$ ) and sulfate/( $\text{SO}_2$ +sulfate) suggested that relatively fresh air masses had been sampled at the study site in the spring season. Comparison of the observed ratios/slopes with those derived from emission inventories showed that while the observed  $\text{SO}_2/\text{NO}_y^*$  ratio (1.29 ppbv/ppbv) in March was comparable (within 20%) to the inventory-derived ratio for the study region, the measured  $\text{CO}/\text{NO}_y^*$  ratio (37 ppbv/ppbv) was about 200% larger. The observed slope of CO relative to NMHC (including ethane, propane, butanes, ethene and ethyne) also indicated the presence of excess CO, compared to the ratios from the inventories. These results strongly suggest that emissions of CO in eastern China have been underrepresented. The findings of this study highlight the importance of characterizing

trace gases and aerosols within source regions of the Asian continent. The springtime results were also compared with data previously collected at the site in 1999-2000, and with those obtained on the TRACE-P aircraft and from a coastal site in South China for the same study period.

## **1. Introduction**

Rapid industrialization in China has stimulated scientific research on possible impacts of the increasing emissions of gases and aerosols on the atmospheric environment and various ecosystems. The emissions of air pollutants have been linked to region-wide pollution such as acid deposition [e.g., Wang and Wang, 1995], photochemical ozone [e.g., Luo *et al.*, 2000; Wang *et al.*, 2001] and regional haze [e.g., Chameides *et al.*, 1999]. Other studies have suggested that Chinese and eastern Asian emissions will potentially affect the tropospheric chemistry and radiative balance over the Pacific Ocean [e.g., Hoell *et al.*, 1996, 1997; Elliott *et al.*, 1997; Jacob *et al.*, 2003; Huebert *et al.*, 2003] and the surface air quality in North America [Jaffe *et al.*, 1999; Jacob *et al.*, 1999].

Emission estimates in the 1990s showed that there was a rapid rise in emissions of anthropogenic pollutants such as NO<sub>x</sub> and SO<sub>2</sub> from the 1980s to the mid 1990s, and a continuing upward trend was projected for the years beyond [e.g., Akimoto and Narita, 1994; Van Aardenne *et al.*, 1999; Streets and Waldhoff, 2000].

However, there is evidence to suggest that energy-use patterns in China began changing quickly in the late 1990s. Recent estimates of emissions [SEPA, 2002; Streets *et al.*, 2003] have shown that between 1995 and 2000 there was a decreasing trend in SO<sub>2</sub> and NO<sub>x</sub> emissions due to the restructuring China's industrial economy, stricter pollution

control measures, and an economic slow-down in the late 1990s. However, it is unclear whether this trend of decreasing emissions – which will be good for the environment – will continue and whether a similar trend is occurring uniformly throughout China. It is therefore crucial that concerted efforts be made to document the trend in emissions and to assess the consequent impact of the changing emissions on the environment.

The measurement of ambient concentrations is integral to understanding the relationship between emissions of pollutants and their environmental impact. Atmospheric concentrations are used to benchmark levels of pollution, document trends in concentration, reconcile emission inventories, elucidate atmospheric processes and constrain chemical transport models. Despite their importance, data on ambient concentrations are sparse in non-urban locations in Asia, particularly in the central and eastern regions of China where large quantities of anthropogenic pollutants are emitted.

*Peng et al.* [1997] and *Luo et al.* [2000] analyzed measurements of O<sub>3</sub> obtained at several rural sites in eastern China in 1994-1995 and found high ozone concentrations in the autumn season. More recently, O<sub>3</sub>, its precursor gases and aerosols were measured at several rural sites in the Yangtze River Delta region as part of a cooperative effort with the China-MAP research project. *Wang et al.* [2001] reported seasonal variations in O<sub>3</sub>, CO, SO<sub>2</sub> and total reactive nitrogen (NO<sub>y</sub><sup>\*</sup>) for 1999-2000 observed at Lin'an and revealed very high concentrations of CO and SO<sub>2</sub>. A follow-up study by *Wang et al.* [2002] found that CO emissions from China could have been underestimated in emission inventories. The study also showed that the burning of biomass/biofuel was a major source of the elevated levels of CO in the autumn-winter period. *Cheung and Wang*

[2001] carried out a detailed analysis of ozone pollution episodes at Lin'an and showed that ozone concentrations were high enough to damage crops grown in the region.

With respect to aerosols, *Xu et al.* [2001] presented fine particulate chemical composition and optical measurements made at Lin'an during November 1999. They found very high loadings of particles at the site. From their organic carbon data, they also found evidence of biomass burning. Prior studies conducted at Lin'an in February and March 1994 as part of the PEM-West program [*Arimoto et al.*, 1997] showed that the concentrations of non-sea salt sulfate there were higher than at Hong Kong, Cheju (Korea), or Okinawa (Japan).

In the present study, we present measurements of trace gases and aerosols obtained at Lin'an in spring 2001. The aim is to better characterize emissions and ambient concentrations in the spring season and to assess the relationship between gases and aerosol pollutants. This field program was conducted during the same period as the ACE-Asia and TRACE-P intensive campaigns over the western Pacific region [*Huebert et al.*, 2003; *Jacob et al.*, 2003]. Our measurements shed light on the characteristics of emissions in the inland Asian continental region, which can aid the interpretation of data collected in downwind locations.

In this paper, we first examine the overall concentrations at Lin'an in spring 2001 and compare these observations with previous results for 1999-2000 and with measurements obtained at a South China coastal site in Hong Kong during the same time period. We then examine the interspecies relationships among the measured trace gases and aerosols, and assess the degree of atmospheric processing using relevant chemical ratios. We reexamine the issue of biomass/biofuel burning and compare the measured

ratios to emission ratios from the latest emission inventories. We also compare our ground-based results with those obtained on the TRACE-P DC-8 and P-3B aircraft.

## 2. Experiment

The study was carried out at the Lin'an Baseline Air Pollution Monitoring Station (30°25'N, 119°44'E, 132 m a.s.l., see Figure 1). A detailed description of the surroundings has been given in *Wang et al.* [2001, 2002]. Only a brief summary is provided here. The site is located in a hilly agricultural/forested area on the southern edge of the Yangtze River Delta. It is 53 km west and 210 km southeast of the major population centers of Hangzhou and Shanghai, respectively. The township of Lin'an (population: ~50,000) is 10 km to the south.

**Continuous measurement of trace gases:** The sampling system and analyzers for measuring O<sub>3</sub>, CO, SO<sub>2</sub>, NO and NO<sub>y</sub>\* employed in the spring 2001 study were identical to those used in our previous measurements at the site [*Wang et al.*, 2002]; thus only a summary is given here. Ambient air was drawn through an 8-m long PFA Teflon tube (inside diameter=9.6 mm) connected to a Teflon-made manifold with a bypass pump. O<sub>3</sub> was measured using a UV photometry instrument (Thermo Environmental Instruments (TEI), Inc., model 49). SO<sub>2</sub> was measured by a pulsed UV fluorescence analyzer (TEI, model 43S). CO was detected with a gas filter correlation, nondispersive infrared analyzer (Advanced Pollution Instrumentation, Inc., model 300) with a heated catalytic scrubber for baseline determination. The zeroing for CO was conducted every 2 hours, with each session lasting 12 minutes.

NO was detected using a chemiluminescence analyzer (TEI, model 42S) with a detection limit of 0.05 ppbv. NO<sub>2</sub> and other reactive nitrogen species were converted to

NO on hot molybdenum oxide maintained at 325<sup>0</sup>C, followed by the quantification of NO using the same chemiluminescence detector. We refer to this measurement as NO<sub>y</sub><sup>\*</sup> because it does not include aerosol nitrate, which was collected on an inline filter placed upstream from the converter. We also note that some nitric acid may have been absorbed in the sample line (despite the short residence time of <2 seconds within the sample line). Filter data have shown that the average fraction of nitrate to NO<sub>y</sub> (the sum of NO<sub>y</sub><sup>\*</sup> and NO<sub>3</sub><sup>-</sup>) during the study period was about 14%, suggesting that there was a relatively minor contribution of NO<sub>3</sub><sup>-</sup> to total reactive nitrogen. The performance of the analyzers was checked on a daily basis by injecting scrubbed ambient air and a calibration standard [Wang *et al.*, 2002]. A data logger was used to control the zero and span tests and to record 1-minute data. Hourly averaged values are presented in this paper.

**Methane, NMHCs, halocarbons and alkyl-nitrates:** Two-liter conditioned, evacuated stainless steel canisters were filled with whole air samples, which were then sent to the University of California at Irvine (UCI) for chemical analysis. Thirty samples were obtained during March 2-April 1, 2001. One sample was collected at noon each day during the above period. Details of the analytical procedures employed at the UCI laboratory for sample analysis can be found in *Colman et al.* [2001] and *Blake et al.* [2002], and are outlined as follows. For each sample, 1285±2 cm<sup>3</sup> (STP) of air was preconcentrated in a liquid nitrogen-cooled loop filled with glass beads. After the preconcentration, the trace gas components were revolatilized using a hot water bath then reproducibly split into five streams, with each stream directed to one of five different gas chromatographic column/detector combinations. Electron-capture detectors (sensitive to halocarbons and alkyl nitrates), flame-ionization detectors (sensitive to hydrocarbons),

and quadrupole mass spectrometers (for unambiguous compound identification and selected ion monitoring) were employed. CO was also quantified from the canister samples by first reducing CO to methane, followed by gas chromatographic analyses with a flame-ionization detector.

**Fine aerosol composition:** Eighteen Teflon filter samples and nine Quartz filter samples were collected every other day during March 10 – April 9, 2001. An Andersen PM2.5 RAAS-2.5-1 ambient air sampler (Thermo Electron Corporation, Waltham, MA) was employed to collect samples, with a flow rate maintained at  $17.6 \text{ L min}^{-1}$ . The sample collection time was approximately 24 hours starting at 09:00. Chemical analyses of the Teflon filters (2  $\mu\text{m}$  pore size and 47 mm diameter, Pall Gelman Inc.) were performed for metal elements, water-extractable metals and ions at the Carlsbad Environmental Monitoring and Research Center of the New Mexico State University.

One half of each Teflon filter was digested for elemental analyses, and the other half was extracted for analyses of anions, cations and water-extractable metals. The elemental analyses were conducted by inductively coupled plasma mass spectroscopy (ICP-MS) using a Perkin-Elmer Elan 6000 unit (Perkin-Elmer Corporation, Norwalk, CT), following EPA Method 200.8. Matrix matching was used to prepare calibration standards for the elemental analyses [Arimoto *et al.*, 2002]. The concentrations of ions were determined using a Dionex 500 ion chromatography system (Dionex Corp, Sunnyvale, CA). Nitrate ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) in the aqueous extracts of both sets of filters were separated using an AS-14 column. Cations were separated using a CS-12A column. Only sodium ( $\text{Na}^+$ ), ammonium ( $\text{NH}_4^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), chloride ( $\text{Cl}^-$ ),  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  were frequently detected on the Teflon filter samples.

Quartz fiber filters (47 mm diameter, Pallflex 2500 QAO, Pall Gelman Inc.) were analyzed for elemental carbon and organic carbon (EC and OC, respectively) at the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) at Georgia Tech. EC and OC were determined using the Thermal-Optical Technique (TOT), which is based on the thermal-optical transmittance properties of a quartz filter containing carbon residue [Baumann *et al.*, 2003]. The analysis proceeded essentially in two stages. First, OC was volatilized from the sample in a pure helium atmosphere as the temperature was stepped from 340 °C to 475 °C to 615 °C to 870 °C within 4.16 minutes. Evolved carbon was catalytically oxidized to CO<sub>2</sub> in a bed of granular MnO<sub>2</sub> (held at ~900 °C), reduced to CH<sub>4</sub> in an Ni/firebrick methanator (~500 °C) and quantified as CH<sub>4</sub> using a flame-ionization detector. During the second stage of the analysis, pyrolysis correction and EC measurement were made. The oven temperature was reduced, an oxygen (10%)-helium mix was introduced, and the oven temperature was then raised from 550 °C to 625 °C to 700 °C to 775 °C to 850 °C to 870 °C within another period of 5.25 minutes. As oxygen entered the oven, pyrolytically generated EC was oxidized and a concurrent increase in filter transmittance occurred. The transmittance was monitored by passing a He/Ne laser light through the filter. The point at which the filter transmittance reached its initial value was defined as the ‘split’ between organic and elemental carbon. Carbon evolved prior to the split was considered ‘organic’, and carbon volatilized after the split was ‘elemental’. The organic carbon concentrations were then multiplied by a factor of 1.4 to account for the mass of hydrogen and oxygen associated with carbon [White and Roberts, 1977; Japar *et al.*, 1984].

**Note on regression analysis:** Much of the data analysis in this paper involves fitting a straight line to the concentrations of a pair of concurrently measured species. Because the two atmospheric variables under consideration are both subject to measurement errors, we have applied a fitting procedure known as the reduced major axis (RMA) method, as described by *Hirsch and Gilroy* [1984]. These authors concluded that RMA is more appropriate than the ordinary least square regression as it more accurately reflects the relationships between geophysical variables. RMA has been used by other researchers in analyzing air quality and atmospheric chemistry data [e.g., *Keene et al.*, 1986; *Arimoto et al.*, 1995; *Freijer and Bloemen*, 2000; *Ayers*, 2001]. We have also tested the level of significance for the regression result, using two-tailed  $t$  tests. Only the regression results with significance levels greater than 95% (i.e.,  $p < 0.05$ ) are shown in plots and used in the discussion.

### **3. Results and discussion**

#### **3.1. Abundance and variations of gases and aerosols**

The synoptic features over eastern Asia in spring 2001 have been discussed in *Fuelberg et al.* [2003]. Figure 1 presents the mean geopotential height and streamlines at 1000 hPa for February 18–April 30, 2001, and shows that there was a predominant northeasterly flow in the boundary layer of southern and eastern China. The plots were made using NCEP/NCAR reanalysis data available at: <http://www.cdc.noaa.gov/cdc/data.ncep.reanalysis.html>. Surface winds at the Lin'an station were, however, light and variable due to the hilly terrain. Frequent cloudy conditions were also observed during the study period. Analysis of previously collected data has shown that strong pollution events at Lin'an were mainly related to the advection

of pollutants from local and sub-regional emissions under weak synoptic winds [Cheung and Wang, 2001].

The statistics of the mixing ratios of the measured constituents are summarized in Table 1. The average mixing ratio was 34 ppbv for ozone, 677 ppbv for CO, 15.9 ppbv for SO<sub>2</sub> and 13.8 for NO<sub>y</sub><sup>\*</sup> during February 18-April 30, 2001. Compared to the same period in the previous year, these levels were 12%, 14%, 16% higher in 2001 for CO, SO<sub>2</sub>, and NO<sub>y</sub><sup>\*</sup>, respectively. In March 2001, when most of the canister and aerosol samples were collected, the monthly mean was comparable for CO (difference=1%) and NO<sub>y</sub><sup>\*</sup> (6%), but was higher for SO<sub>2</sub> (by 14%), compared to March 2000. The average diurnal cycles are shown in Figure 2. They indicate that the mixing ratios of primary pollutants decreased during the daytime, owing to an enhanced dilution of the convective boundary layer. Similar diurnal profiles were observed for these gases in the previous year [Wang *et al.*, 2002] and for the aerosol scattering and absorption coefficients measured in November 1999 [Xu *et al.*, 2001]. O<sub>3</sub> and the NO/NO<sub>y</sub><sup>\*</sup> ratio showed a diurnal cycle typically seen in non-urban locations [e.g., Parrish *et al.*, 1993].

The most abundant NMHC was ethane (mean  $\pm$  s.d = 3189  $\pm$  717 pptv), followed by ethyne (2475  $\pm$  1395 pptv), ethene (1679  $\pm$  1455 pptv) and toluene (1529  $\pm$  1608 pptv). Their mean values were smaller than those obtained in autumn 1999 at the site (ethane=3351  $\pm$  921 pptv, ethyne=2603  $\pm$  880 pptv, ethene=3068  $\pm$  1311 pptv, and toluene=2544  $\pm$  1654 pptv; N=16). Methyl chloride (CH<sub>3</sub>Cl), which was the dominant halocarbon measured, had a mean value of 1108 ( $\pm$  653) pptv compared to 1350 ( $\pm$  430) pptv in autumn 1999. In general, organic species appeared to have lower concentrations in the spring season. For the major components of PM<sub>2.5</sub>, the mean concentration was

21.5  $\mu\text{g}/\text{m}^3$  for organic carbon, 17.3  $\mu\text{g}/\text{m}^3$  for sulfate, 6.5  $\mu\text{g}/\text{m}^3$  for nitrate, 8.7  $\mu\text{g}/\text{m}^3$  for ammonium and 2.5  $\mu\text{g}/\text{m}^3$  for elemental carbon.

During the same time period as studies at Lin'an, trace gases and aerosol elemental compositions were measured at a coastal site (Hok Tsui) in Hong Kong [Wang *et al.*, 2003], which is located southwest of Lin'an (Figure 1). Since the prevailing winds in the South China coastal region are northeasterly in spring, eastern China could be a source region for the air pollutants measured in Hong Kong. Thus, it is of interest to see if the behavior of trace gases measured at the two sites show any relationships. In general, the mixing ratios of the primary pollutants were higher at the eastern China site. For example, the average CO mixing ratio was 677 ( $\pm 315$ ) ppbv at Lin'an versus 404 ( $\pm 228$ ) ppbv at Hok Tsui; SO<sub>2</sub> was substantially higher at Lin'an ( $15.9 \pm 14.6$  versus  $1.8 \pm 3.0$  ppbv); and NO<sub>y</sub> was  $13.8 \pm 7.2$  ppbv at Lin'an compared to  $10.4 \pm 10.7$  ppbv at Hok Tsui. NMHCs and halons also exhibited higher values at the eastern site. The higher concentrations of these substances at the eastern site are expected because of the stronger anthropogenic emissions in the eastern region compared to those in the southern coastal areas.

The ethyne/CO and propane/ethane ratios, which are measures of atmospheric processing [e.g, Smyth *et al.*, 1999], indicated that the air masses sampled at the Hok Tsui site were more 'aged'. As a result, higher mixing ratios of O<sub>3</sub> were observed at the southern site ( $45 \text{ ppb} \pm 19$  at Hok Tsui versus  $34 \pm 18$  ppbv at Lin'an). NO was an exception. Its daytime mixing ratio was higher at the southern site:  $2.7 \pm 8.6$  pptv versus  $0.7 \pm 1.2$  ppbv. The abundant NO and a larger NO to NO<sub>y</sub> ratio at Hok Tsui resulted from fresh emissions of NO<sub>y</sub> from ships in the coastal waters adjacent to the study site [Wang *et al.*, 2003].

Figure 3 compares daily average mixing ratios of ozone and CO at Lin'an and Hok Tsui. While the magnitude and the short-time variability (i.e., hourly to daily) of ozone differed between the eastern and southern sites, the synoptic-scale trends were in phase. We also examined the daytime (08:00-19:59) average of O<sub>3</sub>, which gave a similar synoptic result with a smaller difference in absolute concentration. By contrast, no temporal relationship was shown for CO between the two sites, reflecting the influences of emission and meteorology on a sub-regional scale.

### 3.2. Relationships between trace gases and aerosol composition

Ozone versus CO, NO<sub>y</sub><sup>\*</sup> and SO<sub>2</sub>: In the boundary layer of industrialized regions such as eastern China, ozone is expected to originate primarily from photochemical production involving volatile organic compounds and oxides of nitrogen. Stratospheric intrusion is also known to be at maximum strength in spring [e.g., *Austin and Midgley*, 1994]. Ozone-sonde data at Lin'an in spring 2001 showed that the intrusion was most evident in the upper to middle troposphere above Lin'an, but had no obvious influence on surface ozone concentrations [*Chan et al.*, 2003].

CO is produced from the incomplete combustion of fossil fuel and biomass/biofuel; NO<sub>y</sub> is generated as NO<sub>x</sub> during high-temperature combustion; and SO<sub>2</sub> is mainly produced by burning coals containing sulfur. Positive correlations among O<sub>3</sub>, CO and NO<sub>y</sub> are expected in photochemically 'aged' air masses [e.g., *Trainer et al.*, 1993; *Parrish et al.*, 1998]. We examined the Lin'an data for relationships among these species. Figure 4 shows scatter plots for O<sub>3</sub> versus CO, NO<sub>y</sub><sup>\*</sup> and SO<sub>2</sub> in the afternoon periods (13:00-15:00 local time) during which photochemical activity tends to reach its peak during a day. Some moderately high ozone events (mean hourly O<sub>3</sub> mixing ratio= 60-90

ppbv) were observed in April, but overall, there is a lack of a correlation between  $O_3$  and CO and  $NO_y^*$  ( $r^2=0$  to 0.02), suggesting the mixing of air masses of different photochemical ages and time histories. Removing data points with  $NO/NO_y^*>0.1$  (representing fresh emissions) slightly improved the correlations (see Figure 4). For comparison, we observed strong correlations between  $O_3$  and CO and  $NO_y^*$  in the summer months (June-September) at Lin'an ( $r^2 = 0.64$ ), due to more active photochemistry in summer relative to spring [Wang *et al.*, 2001]. It is interesting to see that  $O_3$  was better correlated with  $SO_2$  than with CO and  $NO_y^*$  (Figure 4) perhaps suggesting that some of the  $O_3$  observed in the spring was transported with  $SO_2$ .

CO versus  $NO_y^*$  and  $SO_2$ : Relationships among CO,  $NO_y^*$ , and  $SO_2$  can provide insights into the sources of these compounds in the study region. Scatter plots of CO,  $NO_y^*$  and  $SO_2$  in spring 2001 show that CO and  $NO_y^*$  were moderately correlated ( $r^2=0.4$ ), but the  $SO_2$ - $NO_y^*$  relationship was more scattered (Figure 5).

To examine the data for temporal trends, the complete data set was stratified by month. A stronger CO- $NO_y^*$  correlation was found in March relative to the full data set. Given that March was the month in which most of the organic samples (29 out of 30) and a majority of the aerosol samples were collected, the data for that month should be most useful in revealing the relationships among the measured species. Figure 6 shows the scatter plots of CO,  $NO_y^*$  and  $SO_2$  in March. The CO- $NO_y^*$  slope was 37 (ppbv/ppbv) with an intercept of 163 and  $r^2$  of 0.59. The slope can be interpreted as the emission ratio while the intercept is the regional background of CO. Similar to the overall data set,  $SO_2$  showed a weak correlation with CO and  $NO_y^*$  in March. This was also observed in our previous study [Wang *et al.*, 2002] suggesting that the  $SO_2$  was either emitted from

sources different from those for CO and  $\text{NO}_y^*$  or that these sources have variable emission ratios of  $\text{SO}_2$  relative to  $\text{NO}_y^*$  and CO.

A comparison of the above results with our data obtained in 1999-2000 [Wang *et al.*, 2002] indicates a smaller CO- $\text{NO}_y^*$  slope in March 2001 than in September-December 1999. The large CO/ $\text{NO}_y^*$  ratios in autumn 1999 (50-70 ppbv/ppbv based on RMA and 30-40 ppbv/ppbv by the ordinary linear regression), together with a strong correlation between CO and the biomass burning tracer  $\text{CH}_3\text{Cl}$ , have been interpreted as indications of the burning of agricultural residues after the summer harvest season [Wang *et al.*, 2002]. In a later section, we will discuss in more detail how the measured slopes compare with emission ratios from the emission inventories, and the extent of biomass burning in spring 2001.

CO versus NMHCs and halocarbons: As previously mentioned, CO is emitted primarily from the incomplete combustion of fossil fuels and by the burning of vegetation. The CO sources also emit some NMHCs and halocarbons (e.g., ethyne from vehicle exhaust) and sometimes co-locate with halocarbon emission sources. The relationship of CO with NMHCs and halocarbons can thus provide useful information on the emission signatures. Figure 7 shows the scatter plots of CO with selected NMHCs and halocarbons. As expected, CO showed a strong correlation with two combustion-related species ethyne ( $\text{C}_2\text{H}_2$ ,  $r^2=0.86$ ) and benzene ( $\text{C}_6\text{H}_6$ ,  $r^2=0.80$ ). It also correlated well with methane ( $\text{CH}_4$ ,  $r^2=0.73$ ), ethane ( $\text{C}_2\text{H}_6$ ,  $r^2=0.78$ ), propane ( $\text{C}_3\text{H}_8$ ,  $r^2=0.77$ ) and ethene ( $\text{C}_2\text{H}_4$ ,  $r^2=0.66$ ). It is interesting to see that CO had a moderate correlation with the biomass burning tracer  $\text{CH}_3\text{Cl}$  ( $r^2=0.59$ ), and also with  $\text{C}_2\text{Cl}_4$  ( $r^2=0.54$ ) and F-11 ( $r^2=0.57$ ), which are primarily released from urban/industrial sources [Wang *et al.*, 1995]. This observation contrasts

with our previous result in autumn 1999, which showed a strong correlation with CH<sub>3</sub>Cl ( $r^2 = 0.83$ ) but a poor correlation with C<sub>2</sub>Cl<sub>4</sub> ( $r^2=0.12$ ) and F-11 ( $r^2=0.11$ ) [Wang *et al.*, 2002]. An examination of the scatter plots of CH<sub>3</sub>Cl versus C<sub>2</sub>Cl<sub>4</sub> and F-11 revealed that CH<sub>3</sub>Cl had a weak correlation with C<sub>2</sub>Cl<sub>4</sub> ( $r^2=0.32$ ,  $p < 0.001$ , not shown), but moderate correlation with F-11 ( $r^2=0.53$ ,  $p < 0.001$ , not shown). Could the latter suggest a strong urban/industrial source for CH<sub>3</sub>Cl in the study region? We compared a few urban samples collected in the Hangzhou metropolitan area and within the township of Lin'an with samples obtained on the same day at the rural Lin'an site. The results showed comparable CH<sub>3</sub>Cl concentrations in the rural and urban areas. For example, in one case, two samples collected in urban Hangzhou showed a CH<sub>3</sub>Cl mixing ratio of 1878 pptv (CO=959 ppbv, from the rooftop of a four-story building) and 2304 pptv (CO=1221 ppbv, collected adjacent to a road), as compared to a mixing ratio of 2212 pptv collected a few hours before at the Lin'an site (CO=944 ppbv). In another case, a sample collected in Lin'an township showed a CH<sub>3</sub>Cl mixing ratio of 1234 pptv (CO=731 pptv), as compared to 1539 pptv (CO=767 ppbv) obtained at the rural site at about same time. These results suggest that rural areas are important source regions for CH<sub>3</sub>Cl, reconfirming the hypothesis that CH<sub>3</sub>Cl is emitted in significant quantities from the burning of biomass/biofuel in rural locations. In conclusion, the correlations of CO with CH<sub>3</sub>Cl, C<sub>2</sub>Cl<sub>4</sub>, and F-11 at Lin'an indicated impact from a combination of biomass/biofuel burning and industrial sources during the spring season. A similar result has been found at the South China site in spring 2001 [Wang *et al.*, 2003].

Table 2 presents the ratios (the slopes of the regressions) of selected NMHCs and halocarbons to CO at Lin'an and Hok Tsui in Hong Kong. The two sites had similar

ratios of  $C_2H_2/CO$ ,  $C_6H_6/CO$  and  $C_2Cl_4/CO$ , while the eastern Lin'an site appeared to have smaller ratios of light alkanes, but a much larger ratio of  $CH_3Cl$  relative to  $CO$ . The large  $CH_3Cl/CO$  ratio at the eastern site implies that the burning of biomass/biofuel produces significant quantities of  $CH_3Cl$ . Table 2 also lists the ratios of some species observed on the TRACE-P DC-8 and P-3B aircraft in air masses originating from source regions such as "South China," "North China" and "Japan +Korea" [Blake *et al.*, 2003]. The ratios of  $C_2H_6$  and  $C_3H_8$  to  $CO$  measured at the site in inland eastern China were lower (by a factor of  $\sim 2.2$ - $2.5$ ) than those observed on the aircraft for air masses originating from industrialized Japan and South Korea. This can be attributed to strong emissions of  $CO$  in China. The site in eastern China also had a much higher (4.7 times) ratio of  $CH_3Cl/CO$ . By contrast, the ratio of  $C_2H_2/CO$  for the Lin'an site was similar to that in the air mass sampled on the TRACE-P aircraft for "Japan + Korea," suggesting that different combustion processes can generate similar  $C_2H_2/CO$  ratios. However, an inconsistent result was found between inland Lin'an and aircraft data for the air mass from "South China" (where Lin'an is located). While the aircraft-observed ratios for  $C_2H_2/CO$  and  $C_3H_8/CO$  from the "South China" region were very close to those observed at the Lin'an site, the ratio for  $C_2H_6/CO$  was a factor of 1.9 lower at the inland site, while the ratio of  $CH_3Cl/CO$  was a factor of 4.2 higher. These results imply that different air masses were sampled at the surface site and on the aircraft.

Interrelationships among aerosol components: As previously mentioned, 18 fine aerosol samples were collected on Teflon filters and analyzed for water soluble ions and trace metals, while another nine samples were collected on quartz filters and examined for organic and elemental carbons. Correlation plots showed that OC and EC were

weakly correlated ( $r^2=0.34$ ), suggesting that they were sometimes emitted from different sources. Ammonium was strongly correlated with sulfate ( $r^2=0.89$ ) and nitrate ( $r^2=0.72$ ), and had a good correlation with potassium ( $r^2=0.61$ ). The ambient levels of ammonium ions were sufficiently high to fully neutralize the sulfates and nitrates (see Figure 8), indicating that large amounts of ammonia resulted from the agricultural practices within the region. This observation contrasts with that of an incomplete neutralization of sulfates and nitrates by ammonia ( $\text{NH}_3$ ) in urban Beijing and Shanghai [Yao *et al.*, 2002]. At Lin'an, fine nitrates were strongly correlated with sulfate ( $r^2=0.70$ ). The large nitrate/sulfate ratios (mean mass ratio=0.42) suggests that the reaction  $\text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) \rightarrow \text{NH}_4\text{NO}_3(\text{s})$  favored the presence of solid-phase ammonium nitrates, probably because of the abundant  $\text{NH}_3$  in the study region. Silicon (Si) in fine aerosols was not well correlated with soil tracers such as aluminum (Al) ( $r^2=0.22$ ), iron (Fe) ( $r^2=0.28$ ), and manganese (Mn) ( $r^2=0.13$ ), but was highly correlated with calcium (Ca) ( $r^2=0.75$ ) and chromium (Cr) ( $r^2=0.83$ ). These results suggest the presence of sources for fine Si and Ca other than soils.

Relationships between gases and aerosols: The concurrent measurements of gases and aerosols in spring 2001 present an opportunity for investigating their relationships. As shown in Figure 9, the time-matched (24-hour average) CO mixing ratio had a good positive correlation with organic carbon ( $r^2=0.65$ ,  $p<0.01$ ) and a moderate correlation with water-soluble potassium ( $r^2=0.53$ ,  $p<0.001$ ), but no correlation with EC ( $r^2=0.04$ ). These results suggested that the major source for CO was the burning of biomass/biofuel in rural areas, but possibly with some contributions from vehicle emissions in urban areas.  $\text{SO}_2$  was correlated with EC ( $r^2=0.56$ ,  $p<0.05$ ) but not OC ( $r^2=0.17$ ), while  $\text{NO}_y^*$  showed

a weak correlation with OC ( $r^2=0.47$ ,  $p<0.05$ ). As expected, the data indicate that SO<sub>2</sub> was produced from the burning of coal.

CO also had moderate to good correlations with secondary aerosol ions such as NH<sub>4</sub><sup>+</sup> ( $r^2=0.62$ ,  $p<0.001$ ) and SO<sub>4</sub><sup>2-</sup> ( $r^2=0.58$ ,  $p<0.001$ ), but SO<sub>2</sub> and NO<sub>y</sub><sup>\*</sup> did not show such relationships. This may suggest that ammonium sulfate and some of the CO were transported to the study site.

Indicators of atmospheric processing: Ambient concentrations can be used to evaluate the extent of photochemical processing and dynamic mixing. This can be done by examining the ratio of a pair of species with different chemical lifetimes, such as C<sub>2</sub>H<sub>2</sub>/CO and C<sub>3</sub>H<sub>8</sub>/C<sub>2</sub>H<sub>6</sub> [e.g., *Smyth et al.*, 1999], or the ratio of a secondary pollutant to the sum of all secondary pollutants and their parent primary pollutant, such as sulfate/total sulfur ( $[\text{SO}_4^{2-}]/[\text{SO}_2]+[\text{SO}_4^{2-}]$ ) and nitrate/total nitrogen ( $[\text{NO}_3^-]/[\text{NO}_y^*]+[\text{NO}_3^-]$ ).

The average ( $\pm$  s.d.) sulfate to total sulfur molar ratio at Lin'an in spring 2001 was 0.24 ( $\pm 0.10$ ), while the nitrate/total nitrogen ratio was 0.14 ( $\pm 0.06$ ). *Ma et al.* [2003] found sulfate/total sulfur ratios of 0.42, 0.51 and 0.89 in three plumes sampled on the TRACE-P P-3B aircraft over the western Pacific rim. The relatively small fraction of sulfate and nitrates at Lin'an compared to those observed on the aircraft indicates that boundary layer air masses at Lin'an were quite fresh with respect to photochemical processing. (The small ratio of nitrate/total nitrogen also implies that our NO<sub>y</sub><sup>\*</sup> measurement (which did not include nitrate particles) was a good representation of total reactive nitrogen (NO<sub>y</sub>)).

The relatively fresh air masses at Lin'an were also indicated by large values of  $C_2H_2/CO$  ( $4.4 \pm 0.8$ , pptv/ppbv) and  $C_3H_8/C_2H_6$  ( $0.38 \pm 0.08$  pptv/pptv). For comparison, *Russo et al.* [2003] reported mean  $C_2H_2/CO$  ratios of 3.9 ( $\pm 1.3$ ) and 2.5 ( $\pm 1.2$ ) in the "Central" and "Coastal" source regions of China, and average  $C_3H_8/C_2H_6$  ratios of 0.35 ( $\pm 0.09$ ) and 0.19 ( $\pm 0.12$ ) in these regions, respectively. Our surface measurements at the South China coastal site showed a mean ratio of 3.9 ( $\pm 0.6$ ) for  $C_2H_2/CO$  and 0.33 ( $\pm 0.08$ ) for  $C_3H_8/C_2H_6$  [Wang *et al.*, 2003].

Because  $C_2H_2/CO$  and  $C_3H_8/C_2H_6$  can serve as measures of atmospheric processing, it is of interest to know how gas concentrations vary with these ratios. One would expect to see higher concentrations of trace gases with the larger values of these ratios (representing fresher air masses). As shown in Figure 10, CO,  $NO_y^*$  and  $SO_2$  had no relationships with  $C_2H_2/CO$  ( $r^2=0.00-0.05$ ). On the other hand, both CO and  $NO_y^*$  showed moderate to good positive correlations with  $C_3H_8/C_2H_6$ , while  $SO_2$  did not. Scatter plots of individual NMHCs also showed strong correlations with  $C_3H_8/C_2H_6$ , but not with  $C_2H_2/CO$ , as illustrated for *n*-butane in Figure 10. These results suggest that  $C_3H_8/C_2H_6$  may be a better measure of atmospheric processing than  $C_2H_2/CO$  for most of the trace gases measured in our study.

### **3.3. On the contribution of biofuel/biomass burning at Lin'an and implications for the refinement of emission inventories**

Previous measurements at Lin'an have shown impacts from biomass burning in autumn and there are indications that total emissions of CO from eastern China have been underestimated. The results are briefly summarized here. Based on the data collected in 1999-2000, we found that the measured  $CO-NO_y^*$  ratio derived from the winter and

nighttime data set was 36 ppbv/ppbv (determined with ordinary linear regression) [Wang *et al.*, 2002]. (The ratio is 46 ppbv/ppbv based on RMA with an uncertainty of 0.8 given as the 95% confidence interval.) This was more than three times the emission ratio derived from an earlier version of the emission inventories of *Streets et al.* [2003] for the year 2000. The previous inventory did not include open biomass burning. We also found that the  $\text{CO}/\text{NO}_y^*$  ratio peaked in September-December 1999 and in June 2000, coinciding with the periods of active open burning of agricultural residues, after the harvesting within the study region of summer rice in autumn and winter wheat in summer. In autumn 1999 we also observed strong correlations of CO with the biomass burning tracer  $\text{CH}_3\text{Cl}$ , and a lack of a correlation with the urban/industrial tracers  $\text{C}_2\text{Cl}_4$  and F-11. We interpreted these observations as indications of crop residue/biofuel burning, and suggested that biomass/biofuel burning could be a major source of the observed CO and possibly of other trace gases as well. An additional indication of biomass burning has also been found from aerosol measurements at the site in November 1999, indicating the existence of a large fraction (~80%) of water-insoluble OC in total OC [Xu *et al.* 2001].

It is of great interest to reexamine the issue of biomass burning for the spring season and to compare the springtime ambient trace gas ratios to those from the latest version of emission inventories developed by *Streets et al.* [2003]. Given that early spring is not a harvesting season, one would expect to see less active open burning of agricultural residues than in autumn. Visual observations during our site visits did indeed indicate less intensive burning in spring 2001, compared with the October-November period in 1999.

Data from the canister samples also revealed a smaller biomass burning signal in spring 2001 than in fall 1999. For example, the NMHC data obtained from March 2-April

1, 2001 showed a weaker correlation of CO with CH<sub>3</sub>Cl and an improved correlation with the industrial tracer of C<sub>2</sub>Cl<sub>4</sub> when compared to the samples from October 26-November 2, 1999. The average CO mixing ratio determined from the canister samples was  $551 \pm 280$  ppbv in spring 2001; this was lower than the average from the autumn 1999 samples ( $686 \pm 204$  ppbv). The lower CO levels and a reduced CO/ NO<sub>y</sub><sup>\*</sup> slope in spring 2001 suggested that there is a smaller impact from the burning of vegetation in spring, which largely can be attributed to the less active burning of crop residues during this season.

How do the ratios observed at Lin'an in spring 2001 compare to the respective ratios derived from the emission inventory of *Streets et al.* [2003] developed for the TRACE-P project for the year 2000? Table 3 shows a comparison of measured SO<sub>2</sub>/NO<sub>y</sub><sup>\*</sup> and CO/NO<sub>y</sub><sup>\*</sup> ratios for the five provinces surrounding Lin'an and the municipality of Shanghai, as well as the regional average. The measured ratios are based on the data for March 2001.

The observed mean SO<sub>2</sub>/NO<sub>y</sub><sup>\*</sup> ratio was 1.29 with an uncertainty of 0.07 at 95% confidence level (all ratios expressed as ppbv/ppbv). This ratio agrees well (within 20%) with the inventory value of 1.08 for the region. This is not too surprising, because the inventory is known to compare well with calculations by other researchers of emissions of SO<sub>2</sub> and NO<sub>x</sub> in China (see discussion in *Streets et al.* [2003]); and emissions in March are believed to be similar to the annual mean according to the seasonality analysis in *Streets et al.* [2003]. In contrast, the observed CO/NO<sub>y</sub><sup>\*</sup> ratio from observations ( $37 \pm 2$ ) is more than twice the inventory value (15.6) for the region. Both the SO<sub>2</sub>/NO<sub>y</sub><sup>\*</sup> and CO/NO<sub>y</sub><sup>\*</sup> ratios are closer to those of the essentially rural province of Jiangxi (1.54 and

25, respectively) than to the urban ratios of Shanghai (0.97 and 9.2). This is perhaps consistent with the location and surroundings of Lin'an.

These ratio results are in accord with our previous comparison of winter 1999 data with the earlier inventory, which found a comparable observed and inventory-suggested  $\text{SO}_2/\text{NO}_y$  ratio (1.37 versus 1.12), but a much larger observed  $\text{CO}/\text{NO}_y$  ratio (44 versus 11). While it is possible that some  $\text{NO}_y$  components (i.e., nitric acid and aerosol nitrate) could have been removed from air masses due to dry and wet deposition before being sampled, thus making our measured  $\text{CO}-\text{NO}_y^*$  slope larger than the original emission ratio, the good linear correlation between CO and  $\text{NO}_y^*$  (Fig. 6) and the relatively 'young' air masses (Fig. 10) at Lin'an in March strongly suggest that the larger observed  $\text{CO}-\text{NO}_y^*$  slope was largely due to an underestimation of CO emissions in the inventory for the study region. We have also found additional evidence for the underestimation of CO by comparing observed NMHC to CO ratios with emission ratios from the inventory (see Table 4). The results show that the observed slopes for ethane, propane, *i*- and *n*- butane, ethene and ethyne are all smaller than the respective emission ratios relative to CO derived from the inventories. This is consistent with the comparison of  $\text{CO}/\text{NO}_y$  ratios, suggesting that CO emissions have been underestimated in the inventories. In particular, the observed ratios of  $\text{CO}/\text{NO}_y^*$ , propane/CO, butane/CO and ethyne/CO suggest that the respective emission ratios would approach the observed values if total CO emissions increased by ~100% for Zhejiang Province.

Under-representation of China's CO emissions has also been found by comparing TRACE-P airborne measurements made over the Yellow Sea with modeled CO concentrations [Carmichael *et al.*, 2003; Palmer *et al.*, 2003] and from a recent global

CO inverse modeling study by *Kasibhatla et al.* [2002]. With the aid of a back-trajectory analysis, *Carmichael et al.* [2003] attributed the under-prediction of CO (and of related species such as SO<sub>2</sub> and BC) in their model to an underestimation of emissions from the domestic use of coal in the central regions of China between Chongqing and Shanghai.

What might be the source of the additional CO observed at Lin'an (and during the TRACE-P flights)? This question is not easy to answer based on the results of our present study. With regard to the inventory, we have conducted several exercises to estimate emission ratios of trace gases by manipulating the inventory of *Streets et al.* [2003]. These exercises include (1) an assumption that 100% of crop residues are burned in two months of the year rather than the inventory value of 17%, (2) a sensitivity analysis of the quantities of biofuel likely to be burned in Zhejiang Province, (3) use of larger emission factors for stoves and small industrial plants such as ovens and kilns, and (4) use of a larger emission factor for transportation. It was concluded that within the range of possible emission factors referenced to literature-reported values and based on the current best estimate of activity data [see discussion in *Streets et al.* 2003], we were unable to identify the missing CO source(s) from the inventory point of view. A systematic survey/test of emission sources (strength and emission ratios) within the study region and in other regions in China will be needed to justify more drastic changes of emission ratios and activity data adopted in the current inventories.

*Carmichael et al.* [2003] suggested that an under-estimation of residential coal burning could be the cause of elevated CO, BC and SO<sub>2</sub> observations during TRACE-P. It is quite possible that recent estimates of residential coal combustion in China are under-reported in national statistics (see discussion in *Streets et al.* [2003]). However,

coal is not a favored residential fuel in the Yangtze delta. Ambient measurements at Lin'an shows that CO had no correlation with the coal burning tracer SO<sub>2</sub> (see Figure 5), which strongly suggests that the majority of CO was not from coal burning within the study region.

What else could cause high concentrations of CO at Lin'an in March? It is known that in Southeast Asia and more remote provinces of China such as Yunnan and Guizhou, March is one of the most significant months for biomass burning. Emissions of CO are very high at this time of year. Is it possible that this is the cause of regional build-up of CO in south-central China? The air-mass dynamics do not seem to support this hypothesis. Most of the high CO events observed at Lin'an were associated with light synoptic winds, suggesting an origin of adjacent or sub-regional sources. Also, sounding data at Lin'an in springtime showed that there was little exchange of air masses between the boundary layer and the free troposphere. In addition, observations showed higher average concentrations of CO at night when a nocturnal stable layer was expected to form, preventing downward transport of air masses. All these indications suggest that the CO was not coming from distant sources.

We have also considered the possibility that the Lin'an measurements may be incompatible with the regional inventory, as the trace gases measured at Lin'an are strongly influenced by sources in rural areas with high CO/NO<sub>y</sub> ratios (such as biofuel and biomass burning) while the regional inventory also includes large urban sources which are expected to have lower CO/NO<sub>y</sub> ratios, as in the case of Shanghai (see Table 4). However, as shown in Wang *et al.* [2002], an examination of the emission ratios in the inventories for rural regions west of Lin'an also indicated a CO/NO<sub>y</sub> ratio about 2-3 times

lower than the observed value at Lin'an. This result confirms that CO emission has been underestimated for rural areas surrounding the study site, and possibly for other rural regions as well. Additional comparisons of regional models with a fine-grid resolution with the measurements at Lin'an will be needed to better understand the missing CO source(s) at Lin'an. It is also essential to survey emission sources in study region and to perform measurements of emissions—whether from stacks, home chimneys, vehicle tailpipes or fields.

#### **4. Conclusions**

We measured trace gases and aerosols at a rural site, Lin'an, in the central-eastern part of China during February 18-April 30, 2001. Overall, trace gas and aerosol levels at this non-urban site were highly elevated, particularly for CO (mean=677 ppbv), SO<sub>2</sub> (15.9 ppbv), organic carbon (21.5 µg/m<sup>3</sup>) and fine-particle sulfate (17.3 µg/m<sup>3</sup>). Given that the land-use pattern surrounding the site is typical of rural regions in eastern China, the results from this study imply widespread regional pollution.

The concurrent measurement of many species yielded important insights about inter-species relationships and emission characteristics in the inland region during the spring season. The results revealed that the sources of pollutants were complex, including the burning of fossil fuels and biomass/biofuels, urban/industrial emissions and agricultural activities. The biomass burning signal was not as strong in spring 2001 compared to previously observations in autumn 1999 [Wang *et al.*, 2002]. Fine sulfate and nitrates were fully neutralized by ammonia, suggesting that a large amount of ammonia resulted from agricultural practices in the region. The measurements also

revealed relatively ‘young’ air masses at the study site, which could undergo photochemical processing as the air masses were transported to regions downwind. The propane to ethane ratio was found to be a better indicator of atmospheric processing, as compared to the ethyne to CO ratio.

Our measurements from eastern China, where large anthropogenic emissions occur, proved to be valuable in validating ‘bottom-up’ emission inventories. Through a comparison of observed versus measured slopes/ratios, CO emissions in the study region were found to have been underrepresented in the current emission inventory. This finding is in accord with our analysis of autumn-winter data previously obtained from this site [Wang *et al.*, 2002]. Additional studies, including a detailed survey of emission sources in the study region and a comparison of ambient data with fine-grid resolution regional models, are required to identify the missing CO source(s) and to investigate its (their) geographical extent.

In view of the complex mixture of chemical signals from different emission sources in non-urban regions of eastern China, studies that combine field measurements with chemical transport models will be needed to elucidate the chemical and transport processes affecting the variations and budgets of trace gases and aerosols. In this connection, our measurements provide an important data set for comparison with modeled results for the central-eastern region of China.

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## Figure captions

- Figure 1 Location of Lin'an in eastern China and mean geopotential height and streamlines for February 18-April 30, 2001. (The plots were made using NCEP/NCAR reanalysis data available at <http://www.cdc.noaa.gov/cdc/data.ncep.reanalysis.html>). A South China coastal site (Hok Tsui) in Hong Kong, against whose data the Lin'an data are compared, is also shown.
- Figure 2 Average diurnal variations of  $O_3$ , CO,  $NO_y^*$ ,  $SO_2$ , and  $NO/NO_y^*$  at Lin'an during February 18-April 30, 2001.
- Figure 3 Daily average mixing ratios of ozone and CO measured at Lin'an and Hok Tsui during February 18-April 30, 2001.
- Figure 4 Scatter plots for  $O_3$  versus CO,  $NO_y^*$  and  $SO_2$  for 13:00-15:00 during February 18-April 30, 2001 at Lin'an.
- Figure 5 Scatter plots of CO,  $NO_y^*$  and  $SO_2$  during February 18-April 30, 2001 at Lin'an.
- Figure 6 Scatter plots of CO,  $NO_y^*$  and  $SO_2$  in March 2001 at Lin'an.
- Figure 7 Scatter plots of CO and selected NMHCs and halons collected between March 2 and April 1 2001 at Lin'an.
- Figure 8 Scatter plots of ammonium versus the sum of nitrate and sulfate.
- Figure 9 Scatter plots of CO,  $NO_y^*$  and  $SO_2$  and time-matched OC, EC,  $K^+$  during spring 2001.
- Figure 10 Scatter plots of CO,  $NO_y^*$ ,  $SO_2$ , and *n*-butane with  $C_2H_2/CO$  and  $C_3H_8/C_2H_6$ .  
 $C_2H_2$  = ethyne;  $C_3H_8$  = propane;  $C_2H_6$  = ethane.

### **Table captions**

- Table 1 Statistics of trace gases and aerosols observed at Lin'an during February 18 - April 30, 2001.
- Table 2 Slopes of selected NMHCs and halons versus CO at Lin' an, Hok Tsui (Hong Kong) and from TRACE-P aircraft data collected in spring 2001.
- Table 3 Comparison of emission ratios and the observed ratios for CO, NO<sub>y</sub><sup>\*</sup> and SO<sub>2</sub> at Lin'an in March 2001.
- Table 4 Comparison of observed NMHC/CO slopes with ratios from the inventories for different source categories for Zhejiang province.

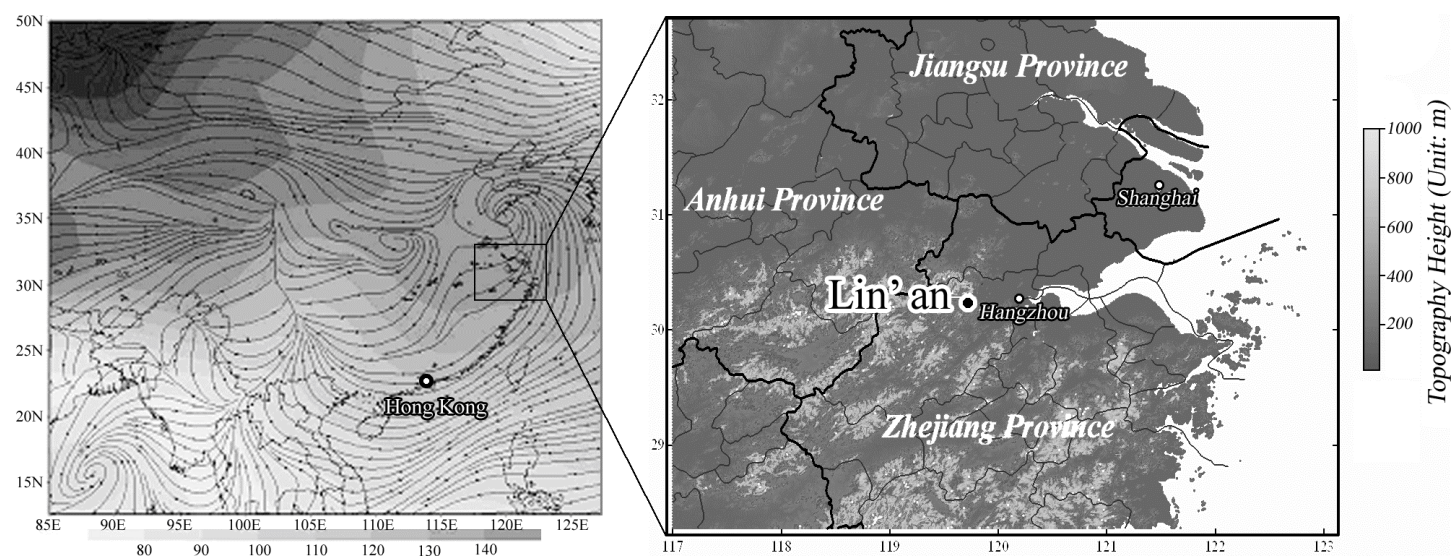


Figure 1.

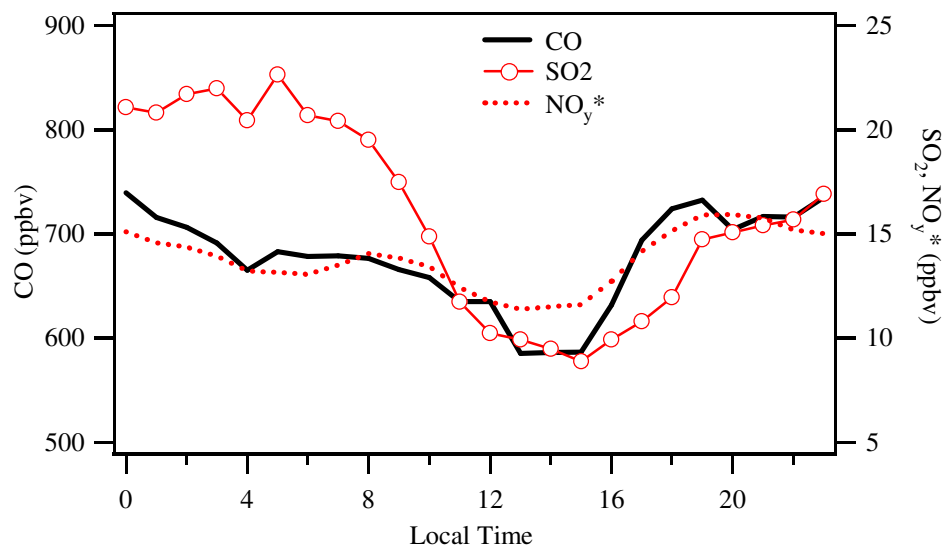
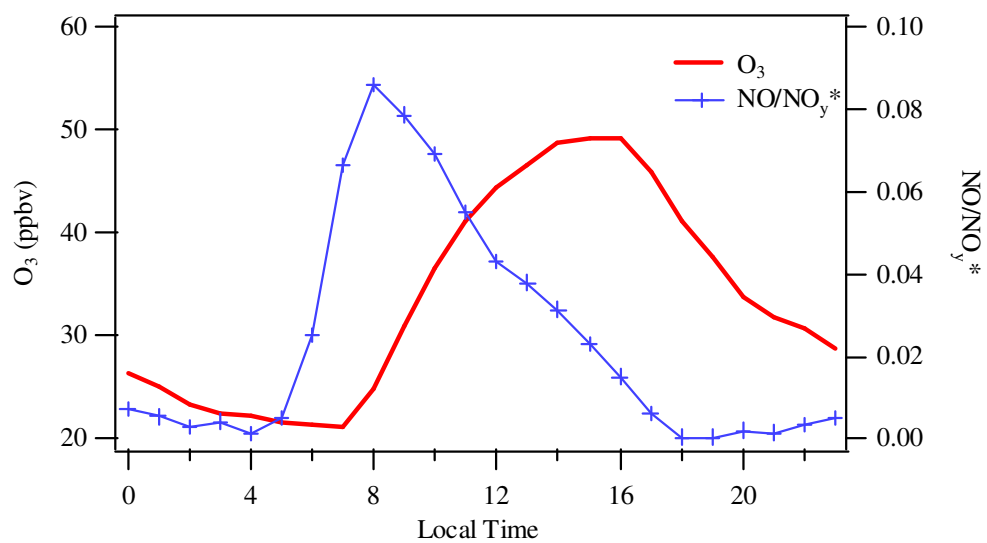


Figure 2

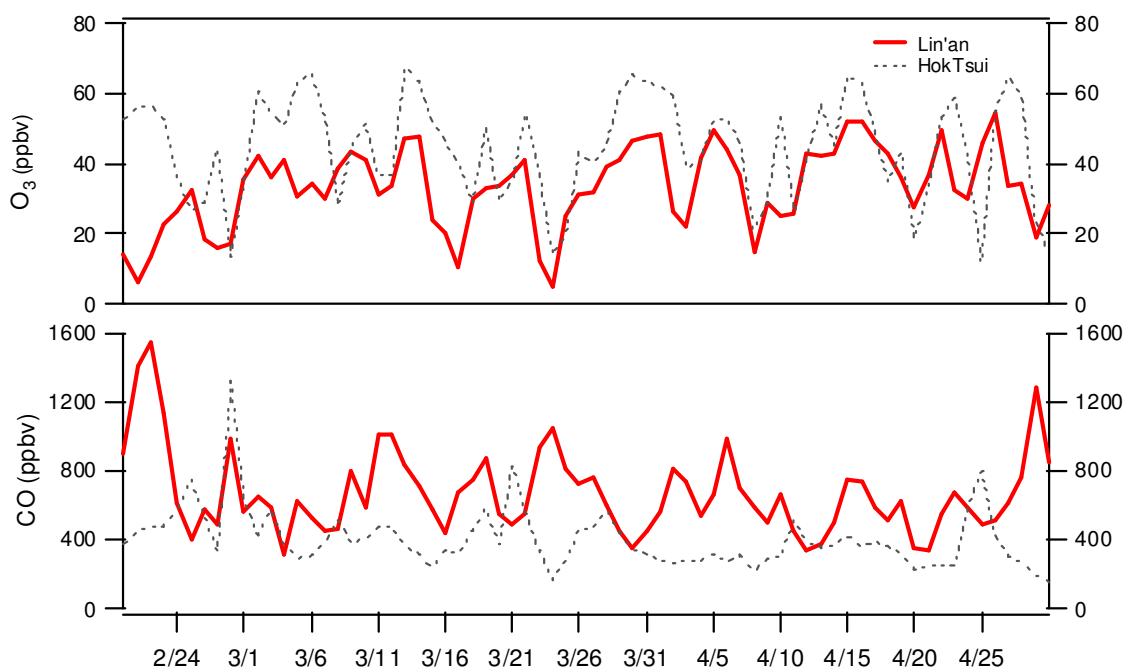


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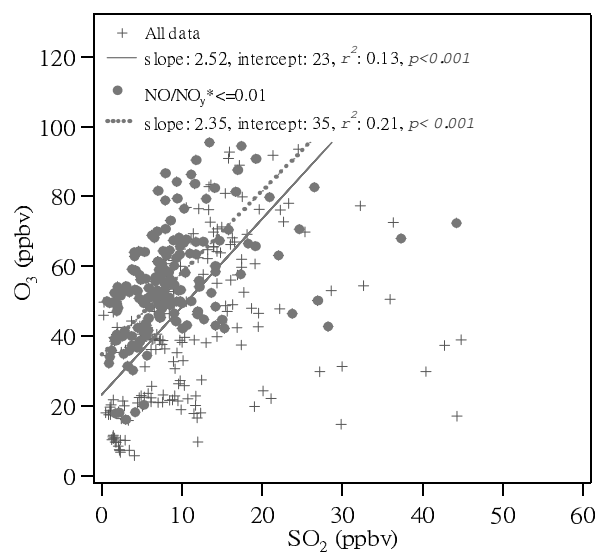
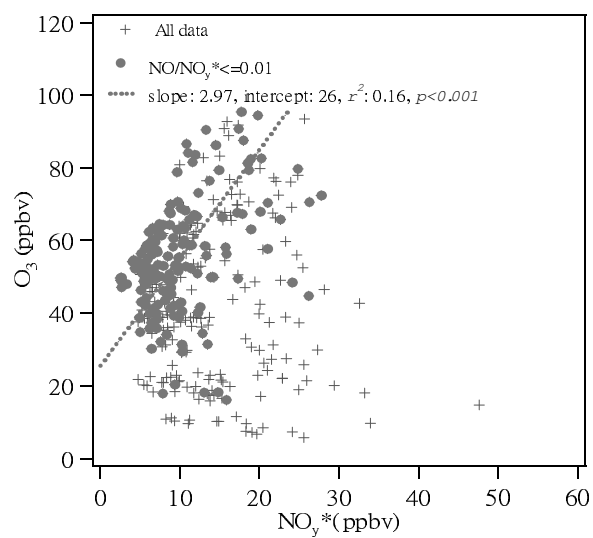
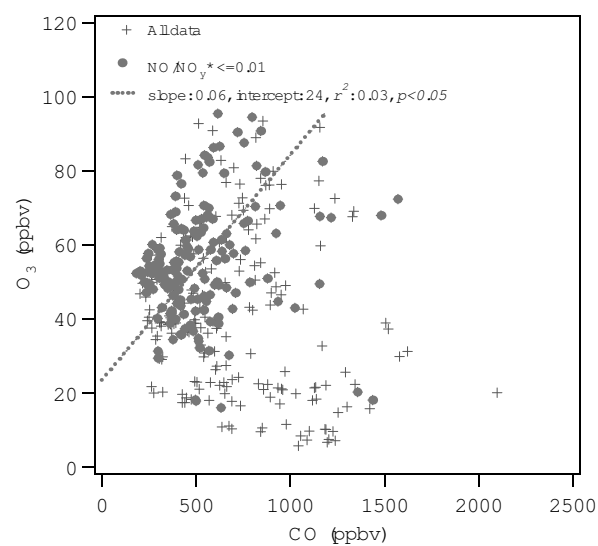


Figure 4.

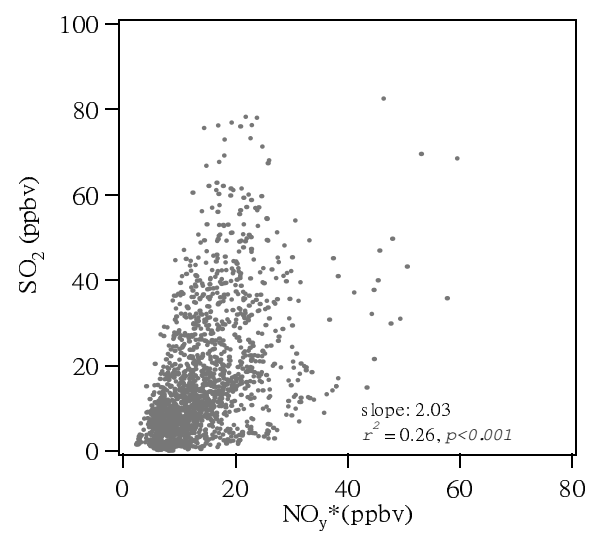
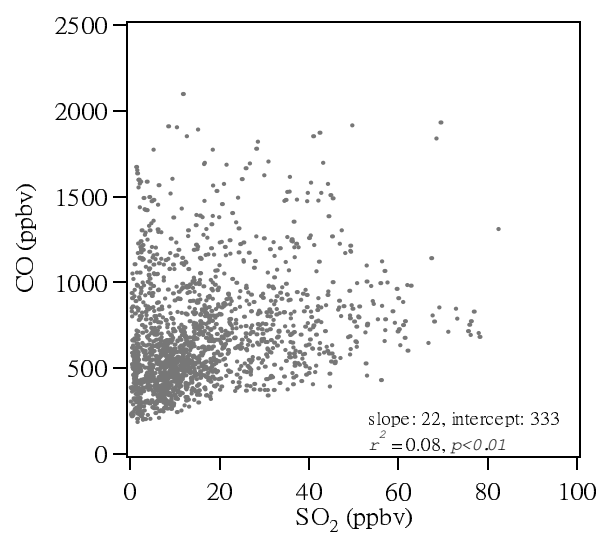
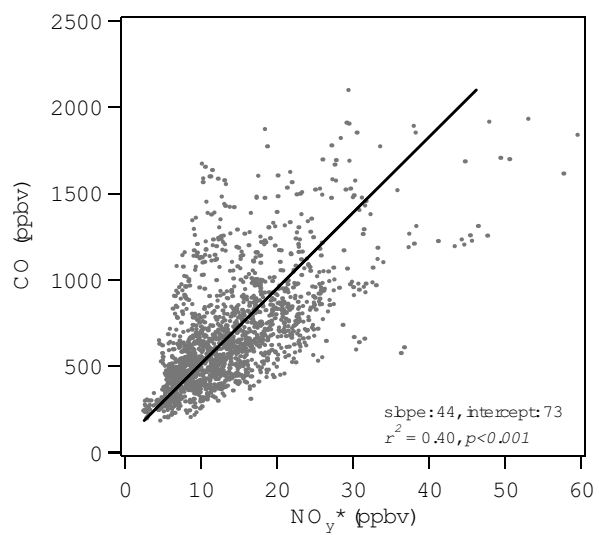


Figure 5.

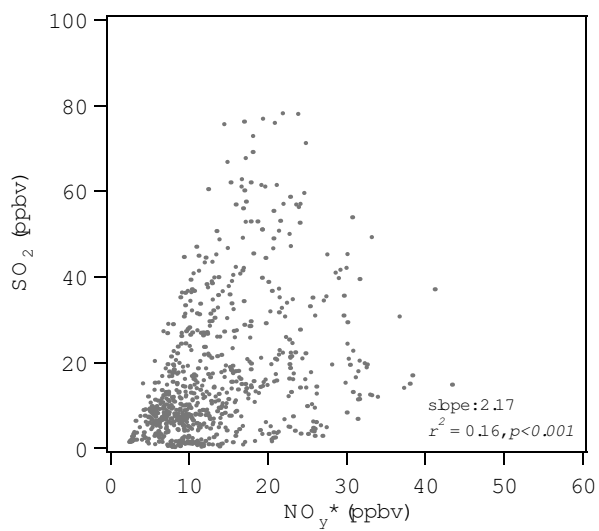
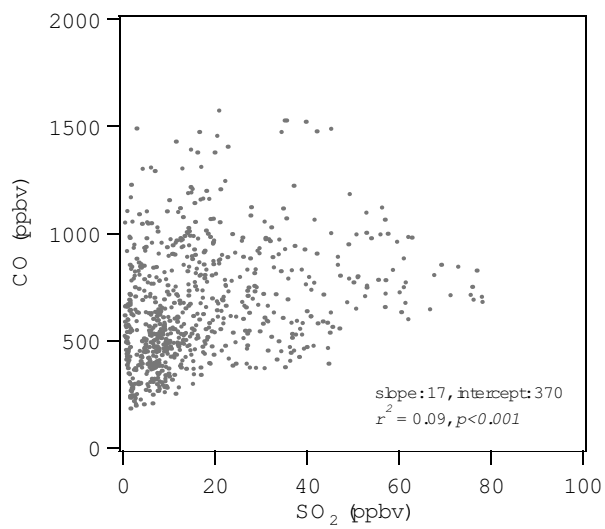
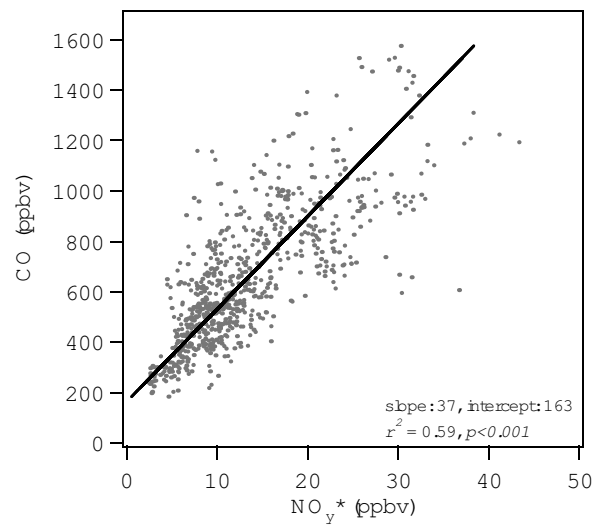


Figure 6.

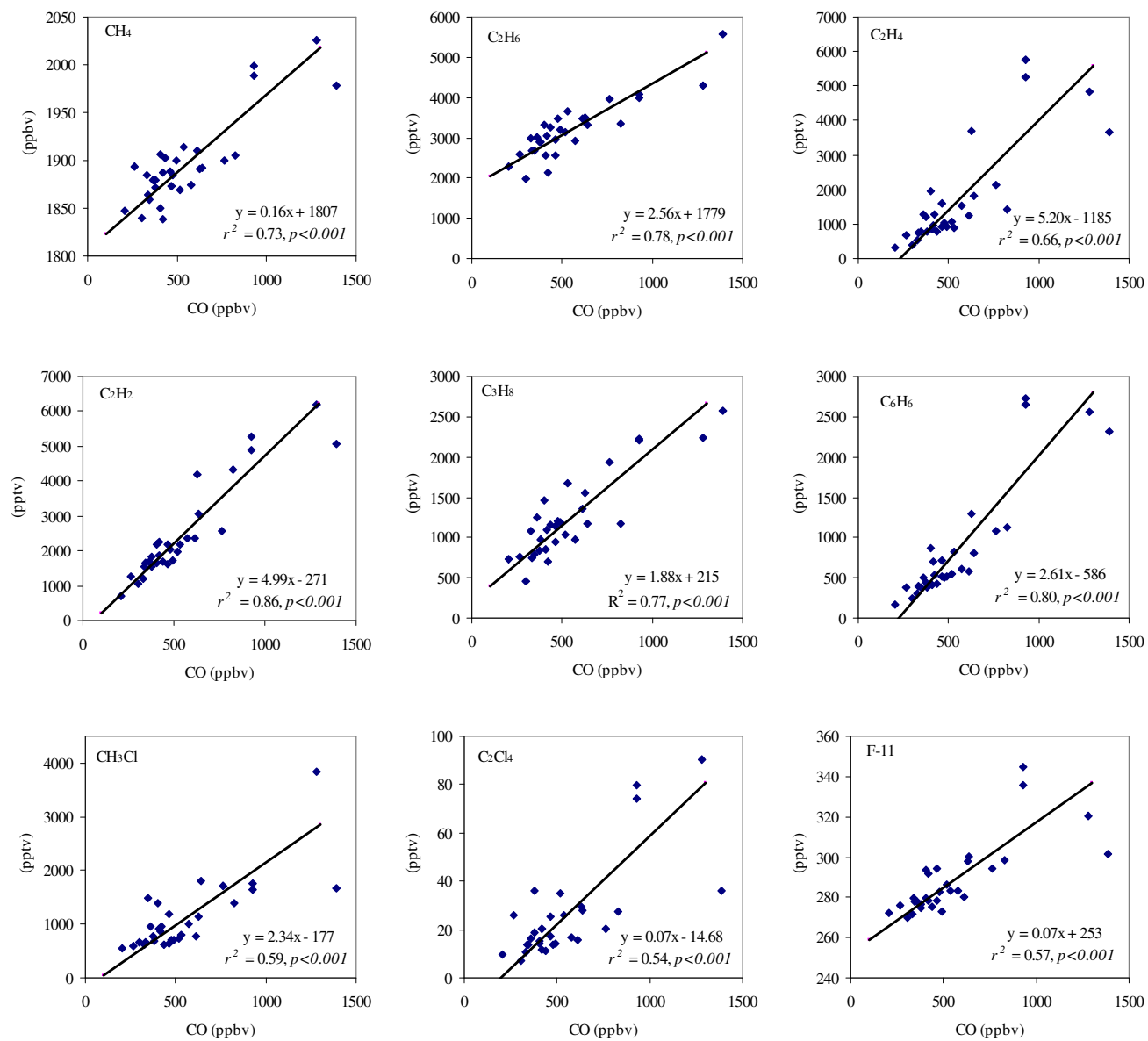


Figure 7.

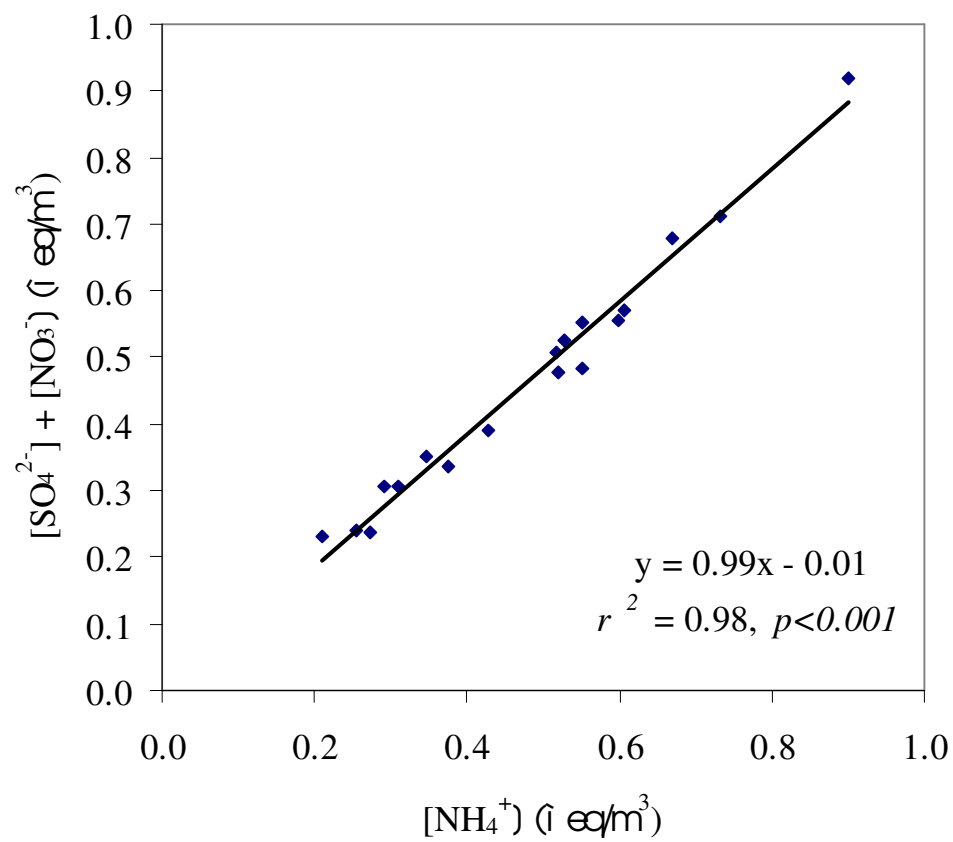


Figure 8.

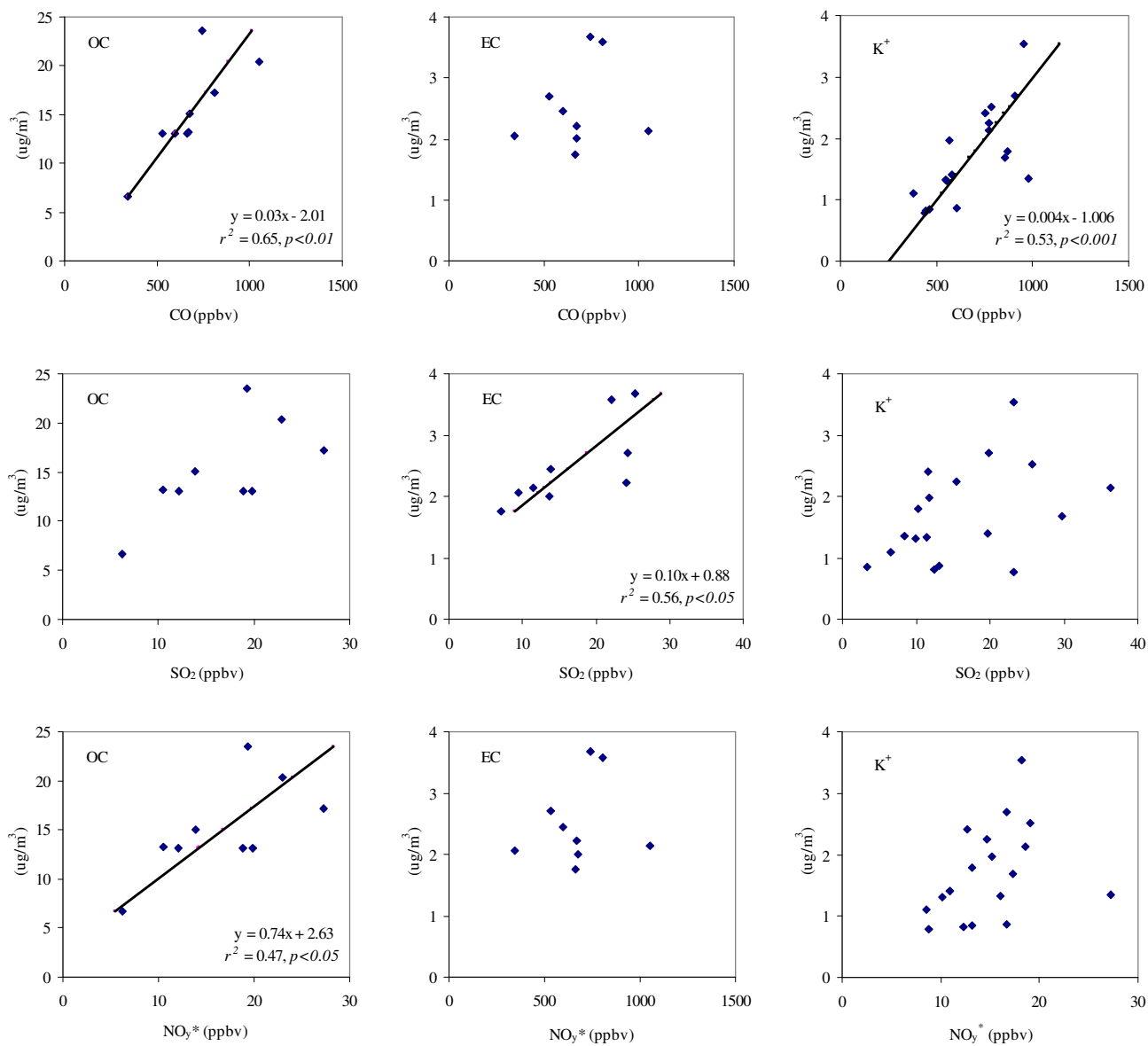


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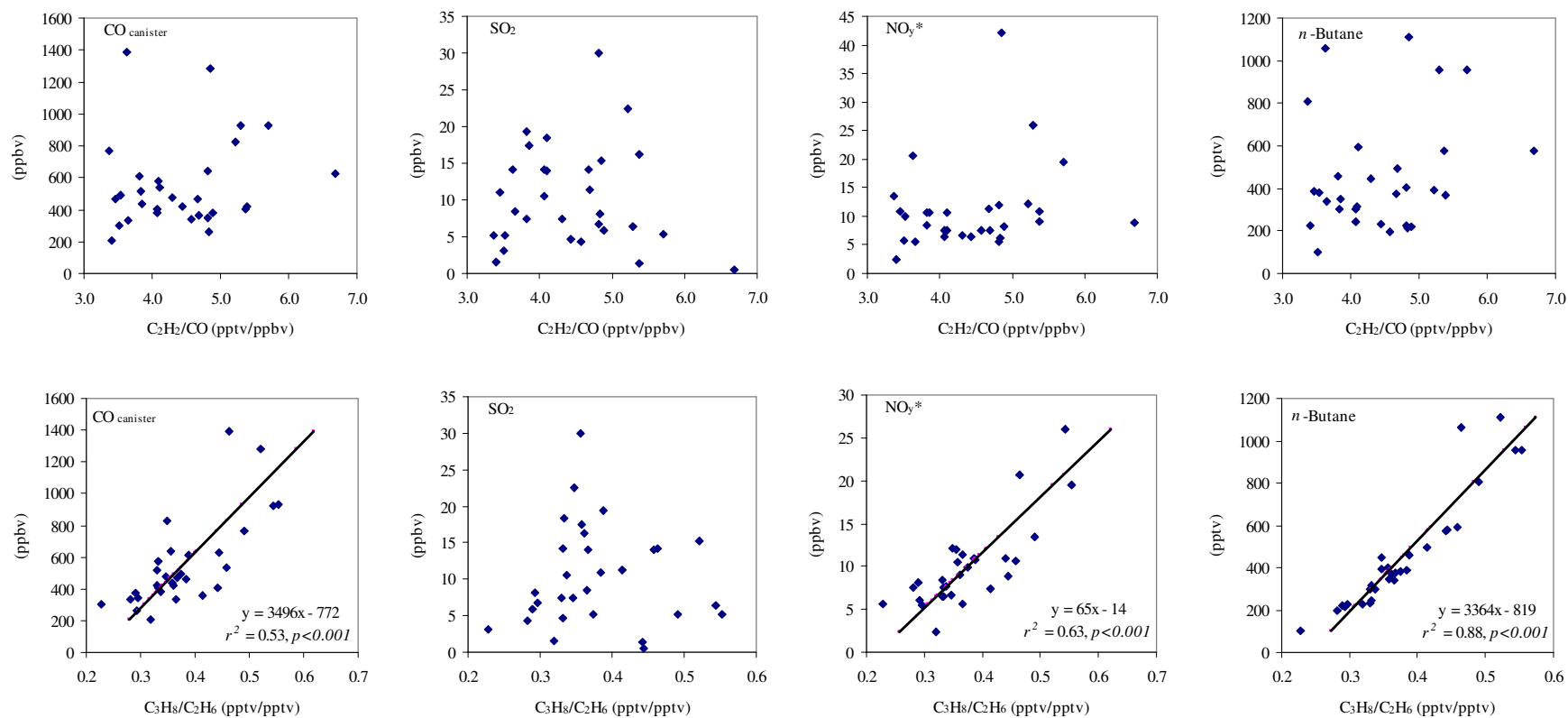


Figure 10.

**Table 1.** Statistics of trace gases and aerosols observed at Lin' an during February 18April 30, 2001

		Average	Std	Median	Max	Min	N
<u>Continuously measured trace gases</u>							
O <sub>3</sub>	(ppbv)	34	18	32	95	1	1709
CO		677	315	604	2098	183	1708
SO <sub>2</sub>		15.9	14.6	11.4	82.5	0	1708
NO <sup>a</sup>		0.7	1.2	0.3	9.3	0	854
NO <sub>y</sub> <sup>*</sup>		13.8	7.2	12.2	59.5	2.4	1708
<u>Methane and Non-methane NMHCs<sup>b</sup></u>							
CH <sub>4</sub>	(ppmv)	1.896	0.045	1.888	2.025	1.839	30
Ethane	(pptv)	3189	717	3084	5565	1978	30
Propane		1250	526	1149	2580	452	30
<i>i</i> -Butane		403	296	294	1273	73	30
<i>n</i> -Butane		453	269	378	1113	99	30
<i>i</i> -Pentane		345	334	231	1385	53	30
<i>n</i> -Pentane		140	133	91	489	24	30
Ethene		1679	1455	1148	5741	317	30
Propene		298	314	176	1270	41	30
1-Butene		73	69	51	268	5	30
Ethyne		2475	1395	2018	6205	705	30
Benzene		851	730	542	2732	175	30
Toluene		1529	1608	860	6900	74	30
Ethylbenzene		200	171	131	643	15	30
<i>m</i> -Xylene		295	274	260	1112	15	30
<i>p</i> -Xylene		203	177	189	660	9	30
<i>o</i> -Xylene		194	159	188	571	12	30
Isoprene		69	172	22	938	2	30
<u>Halocarbons</u>							
F-11		288	18	281	345	270	30
F-12		571	15	568	600	542	30
F-113		87	8	86	122	81	30
HCFC 22		180	27	172	254	147	30
CH <sub>3</sub> Cl		1108	653	891	3829	544	30
CH <sub>3</sub> Br		14	7	11	45	9	30
Ethyl Chloride		22	16	16	59	7	30
CCl <sub>4</sub>		111	11	108	147	100	30
C <sub>2</sub> Cl <sub>4</sub>		26	21	18	90	7	30
CH <sub>2</sub> Cl <sub>2</sub>		83	75	54	419	31	30
MeCCl <sub>3</sub>		47	3	47	52	41	30
CHCl <sub>3</sub>		52	104	23	576	11	30
1,2-DCE		82	113	38	487	10	30
<u>Major PM<sub>2.5</sub> Composition</u>							
OC	( $\mu\text{g m}^{-3}$ )	21.5	7	18.9	33.7	9.5	9
EC		2.5	0.7	2.2	3.7	1.8	9
SO <sub>4</sub> <sup>2-</sup>		17.3	6.6	16.5	33.6	8.1	18
NO <sub>3</sub> <sup>-</sup>		6.5	4	6.3	15.6	0.5	18
NH <sub>4</sub> <sup>+</sup>		8.7	3.3	9.3	16.2	3.8	18
Na <sup>+</sup>		0.2	0.1	0.2	0.4	0.1	18
K <sup>+</sup>		1.7	0.8	1.5	3.5	0.8	18
Mg <sup>2+</sup>		0.3	0.1	0.2	0.5	0.2	12
Cl <sup>-</sup>		1	0.3	1	1.7	0.5	18

<sup>a</sup> only data taken between 06:00 and 17:00 were used for the NO statistics here.

<sup>b</sup> NMHCs and halons were determined from whole air samples collected from March 2 to April 1, 2001; aerosol samples were collected during a 24-hour period from March 10 to April 9, 2001.

**Table 2.** Slopes of selected NMHCs and halons to CO at Lin' an, Hok Tsui (Hong Kong) and from TRACE P aircraft in spring 2001.

	C <sub>2</sub> H <sub>6</sub> /CO	C <sub>2</sub> H <sub>2</sub> /CO	C <sub>3</sub> H <sub>8</sub> /CO	C <sub>6</sub> H <sub>6</sub> /CO	CH <sub>3</sub> Cl/CO	C <sub>2</sub> Cl <sub>4</sub> /CO
Linan	2.6 ± 0.46	5.0 ± 0.72	1.9 ± 0.35	2.6 ± 0.45	2.3 ± 0.58	0.07 ± 0.02
Hok Tsui <sup>a</sup>	4.8 ± 1.19	5.5 ± 0.57	2.9 ± 0.74	2.3 ± 0.46	1.1 ± 0.33	0.08 ± 0.02
<b>TRACE-P<sup>b</sup></b>						
‘S.China’	4.9	4.7	1.8	-	0.54	-
‘N.China’	3.4	3.8	1.1	-	0.34	-
‘Japan + Korea’	6.5	4.7	4.2	-	0.50	-

<sup>a</sup> Wang *et al.* (2003), <sup>b</sup>Blake *et al.* (2003)

Uncertainties are given as 95% confidence intervals

**Table 3.** Comparison of emission ratios and the observed ratios for CO, NO<sub>y</sub>\* and SO<sub>2</sub> at Lin'an in March 2001.

	SO <sub>2</sub> /NO <sub>y</sub> <sup>*</sup>	CO/NO <sub>y</sub> <sup>*</sup>
Zhejiang	0.88	13
Shanghai	0.97	9
Jiangsu	1.24	14
Jiangxi	1.54	25
Fujian	0.83	22
Anhui	0.92	19
Region average	1.08	16
Measurement inferred	1.29 ± 0.07 <sup>a</sup>	37 ± 2

<sup>a</sup> Measured value is the average concentration ratio for SO<sub>2</sub>/NO<sub>y</sub>\* and the regression slope for CO/NO<sub>y</sub>\*.

Uncertainties are given as 95% confidence intervals.

**Table 4.** Comparison of observed NMHC/CO slopes with ratios from the inventories for different source categories for Zhejiang province.

	Ethane/CO	Propane/CO	Butanes/CO	Pentanes/CO	Ethene/CO	Propene/CO	Ethyne/CO	Benzene/CO
BioB	10.7	3.9	0.4	0.1	16.5	7.9	4.6	0.6
Anthro	7.7	4	4.2	2.8	16.9	4.5	9.7	2.4
BioB + Anthro	8	4	3.8	2.5	16.9	4.8	9.3	2.3
Measurement inferred at Lin' an								
Slope	2.6 ± 0.46	1.9 ± 0.35	2.0 ± 0.33	1.7 ± 0.33	5.2 ± 1.17	1.1 ± 0.28	5.0 ± 0.72	2.6 ± 0.45

BioB=Biomass burning, Anthro=Anthropogenic

Uncertainties are given as 95% confidence intervals.